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Depletion potential between large spheres immersed in a multicomponent mixture of small spheres

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We analyze the depletion potential between large spheres in a multicomponent mixture of dense small spheres (up to seven components) using the integral equation theory (IET), in which semiempirical bridge functions are incorporated, and the insertion approach within the framework of density functional theory (DFT). The diameters of the small spheres considered are in the range of d_S – $5d_S$. The results from the IET and DFT are in close agreement with each other. The depletion potential in the mixture is substantially different from that in a one-component system of dense small spheres with diameter d_S . In comparison with the latter, the former possesses in general a less pronounced oscillatory structure, and the free-energy barrier for large spheres to overcome before reaching the contact is significantly reduced. This tendency can be enhanced as the number of components increases. In a several-component mixture of small spheres whose diameters are suitably chosen and in which the packing fractions of the components share the same value, the depletion potential is essentially short ranged and attractive and possesses a sufficiently large, negative value at the contact. © 2006 American Institute of Physics. [DOI: 10.1063/1.2345200]

I. INTRODUCTION

The depletion effect, which is purely entropic in origin, has received much attention in a variety of fields such as soft-matter physics, biophysics, and colloidal science. The simplest but important quantity that has extensively been studied is the depletion potential (i.e., an entropically induced interaction) between large spheres^{1–3} or between a large sphere and a planar wall surface^{4–6} immersed in small spheres. The lateral depletion force acting on a large sphere on a surface with changing geometry has also been investigated rather extensively in theories^{6–10} and experiments.¹¹ It is experimentally known that the depletion effect causes phase separation phenomena for small/large colloidal particles in the bulk and at surfaces.^{12,13} We note that the small spheres considered in those theoretical and experimental studies have the same size and form a one-component system.

The depletion potential is greatly influenced by the packing fraction of small spheres. As the packing fraction increases, the contact value of the depletion potential becomes lower (i.e., the stabilization free energy becomes larger), whereas the free-energy barrier for large spheres to overcome before reaching the contact becomes higher. The barrier is closely related to the kinetics. Experimental studies have shown that the barrier can often be so high that the contact of large spheres hardly occurs. For a binary mixture of large and small colloidal particles in suspension, if the packing fraction of large particles and/or that of small ones

are sufficiently high, a crystalline phase of large particles is deposited at a flat surface.^{12,13} In the case of a very high packing fraction of small particles, however, it can take more than two days for the phase separation to occur or no phase separation can be observed.¹³ Another example experimentally observed for the binary mixture is that large particles come together only rarely when the packing fraction of small ones is considerably high.¹⁴

It has been suggested for a binary mixture of large and small colloidal particles that the motion of large particles can be controlled using passive surface microstructures creating localized entropic force fields that repel or trap the particles and induce their drift in a predetermined direction.¹¹ Manipulation techniques based on these effects are expected to be useful for the production of highly ordered particle arrays. For example, a microscopic circular terrace can be used to trap a large particle that will be attracted vertically to the flat surface and constrained laterally by the step-edge barrier. An array of such terraces could be used to make the big particles self-assemble in a chosen pattern. This suggestion was made within the framework of Asakura-Oosawa (AO) approximation.^{15,16} Due to the nature of the AO approximation, which treats the small particles as an ideal gas, the predicted depletion potential possesses no free-energy barrier against the stabilization occurring when the particle touches the surface or it is trapped in a corner. The real entropic force is more complicated in the sense that it is oscillatory and characterized by the free-energy barriers playing important roles. It is interesting to ask how the depletion potential can be engineered such that the barriers are reduced while the stabilization free energy is kept sufficiently large.

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Some earlier studies considered a multicomponent system of small spheres^{17–24} to calculate the depletion potential between large spheres. Goulding and Hansen¹⁷ reported that the size polydispersity of small spheres has little effect on the depletion attraction but damps the subsequent oscillations in the depletion potential. Kinoshita¹⁸ found remarkably large effects due to the addition of a small amount of medium spheres to small ones. Henderson and co-workers^{19–22} and Akiyama *et al.*²³ studied the depletion potential between large spheres in medium spheres and emphasized large changes of the potential caused by the introduction of small spheres. In these studies, the medium spheres are much larger than the small ones. Kinoshita *et al.*²⁴ treated the depletion potential between large spheres in a binary mixture of small spheres. It was shown that the range of the depletion potential in the mixture is considerably shorter than that in a one-component system of small spheres, because the amplitude of the oscillation is strongly damped except at small separations. However, no significant reduction of the free-energy barrier was found.

It was shown⁵ that the oscillatory structure in the depletion potential is closely related to the asymptotic decay of the bulk correlation functions of the system of small spheres. In a one-component hard-sphere fluid, the asymptotic decay is an exponentially damped oscillation with the wavelength set by the diameter of the small spheres. In mixtures of spheres with sufficiently different diameters, it can be shown^{25,26} that the oscillatory structure displays a richer behavior than its one-component counterparts. From the structure of the Ornstein-Zernike equations for short-ranged interactions, one finds that there is a unique wavelength in all the correlation functions of the mixture and that this wavelength can jump discontinuously^{25,26} when a line, the so-called structural crossover line, in the phase diagram is crossed. Thus, studies on the depletion potential in mixtures of small spheres still present much challenge.

We expect that an answer to the question raised above can be given when large spheres are immersed in a multicomponent mixture comprising small spheres with different sizes. The depletion force between large spheres originates from the nonuniformity of the thermal pressure due to small spheres acting on the large-sphere surfaces. When all the small spheres have the same diameter d_s , the net force becomes repulsive close to $r - d_L \sim md_s$ (in this article r denotes the distance between centers of the spheres considered, d_L is the diameter of large spheres, and $m = 1, 2, \dots$) and attractive otherwise. For $r - d_L \sim md_s$, the small spheres are more densely packed within the confined domain (i.e., the space confined between the large-sphere surfaces) than in the bulk, giving rise to a repulsive net force. Otherwise, the small spheres within the confined domain are not as dense as in the bulk (i.e., a number of small cavities are formed), leading to an attractive net force. When the small spheres have different sizes ($\geq d_s$), however, both the dense packing and the cavity formation should significantly be damped. As a consequence, the oscillations of the depletion force and potential are also damped. Still, for $r - d_L < d_s$, since no small spheres are

present within the confined domain, the net force induced is expected to be strongly attractive, leading to a sufficiently large free-energy decrease at the contact.

The investigation of the depletion potential in a multicomponent mixture is important from another viewpoint. It has been shown that the translational entropy of water plays critical roles in a variety of biological processes.^{7–9,27–34} In the biological systems, the small spheres correspond to water molecules and the large ones to macromolecules.^{10,23} However, there are always many other molecules which are smaller than macromolecules but larger than water molecules. Therefore, it is interesting to analyze the depletion potential between large spheres immersed in a multicomponent mixture comprising small spheres with different sizes.

In this article, we investigate theoretically the depletion potential between large spheres in a multicomponent mixture of small spheres (up to seven components). Since there are no computer simulation data to be compared with our results, we employ two theories, the integral equation theory^{1,24,35} (IET) in which semiempirical bridge functions are incorporated and the density functional theory^{5,6,9,27,32,36–38} (DFT). These are capable of calculating the depletion potential between large spheres immersed in an arbitrary number of components. It is verified that the results from the two different routes are in close agreement with each other. At the same time, we show that the results from the hypernetted-chain approximation without the bridge functions exhibit significant deviations. The depletion potential is remarkably different from that in a one-component system of small spheres.

II. MODEL AND THEORY

A. Model

The entropic effect is omnipresent in molecular systems and essential in dense fluids. In the analysis of the depletion potential, an entropically induced interaction, the hard-sphere model is usually employed, because in this model system all the allowed configurations share the same energy and the system behavior becomes purely entropic in origin. Therefore, we also employ the hard-sphere model to exclusively investigate the entropic effect.

Large spheres with diameter $d_L = 10d_s$ are immersed in an M -component mixture of small spheres with diameters d_i ($i = 1, \dots, M$) in the range of $d_s \leq d_i \leq 5d_s$ and packing fraction η_i . The large spheres are present at the infinite dilution limit $\eta_L \rightarrow 0$. The total packing fraction of the mixture is kept at 0.400. We examine a total of eight systems whose specifications are summarized in Table I. As discussed by Kinoshita *et al.*,²⁴ the depletion potential between large spheres is influenced by the packing of small spheres within the space confined between the large-sphere surfaces. According to their discussion, the amplitude of the oscillation in the depletion potential in a binary mixture is damped to the largest extent when the two components share almost the same packing fraction (not the same mole fraction). Following this result, we set the packing fractions of the components at the same value.

TABLE I. Eight systems considered. In system 7, for example, the packing fractions of small spheres with diameters d_s , $1.5d_s$, $2d_s$, $2.5d_s$, $3d_s$, $3.5d_s$, and $4d_s$ are 0.058, 0.057, 0.057, 0.057, 0.057, 0.057, and 0.057, respectively. The total packing fraction is kept at 0.400 in all the systems.

System	d_s	$1.5d_s$	$2d_s$	$2.5d_s$	$3d_s$	$3.5d_s$	$4d_s$	$5d_s$
1	0.400
2	0.400
3	0.200	0.200
4	0.200	...	0.200
5	0.200	0.200	...
6	0.100	...	0.100	...	0.100	...	0.100	...
7	0.058	0.057	0.057	0.057	0.057	0.057	0.057	...
8	0.080	...	0.080	...	0.080	...	0.080	0.080

B. Integral equation theory (IET)

The computer (e.g., molecular dynamics) simulations can hardly be applied to the calculation of the depletion force (or potential) between large particles immersed in a mixture of small and medium particles. First, two large particles separated by a prescribed distance are immersed in the mixture, and the average force induced between the large particles is calculated. When the size asymmetry of the mixture is high as in the present study, however, the basic cell required is unacceptably large and obtaining a sufficiently accurate ensemble-averaged force becomes a formidable task. Moreover, a number of different distances between the large particles must be considered in separate simulations in order to calculate the mean-force curve. By contrast, the IET allows us to obtain the whole curve of the potential of mean force only by one calculation with very minor computational effort.

The basic equations were described in earlier publications.^{1,24,35} The Ornstein-Zernike integral equation is coupled with a closure equation. In this article, we employ the hypernetted-chain (HNC) closures and modified closures with semiempirical bridge functions. The IET employing the modified closures is referred to as the MHNC theory.

Among various functional forms, the semiempirical bridge function proposed for hard-sphere fluids by Verlet³⁹ is very simple and convenient. It relates the bridge function $b(r)$ to the correlation function $\gamma(r)=h(r)-c(r)$ (h and c denote, respectively, the total and direct correlation functions) simply by

$$b(r) = -0.5\{\gamma(r)\}^2/\{1 + 0.8\gamma(r)\}. \quad (1)$$

However, Eq. (1) has a singularity at $\gamma=-1/0.8$ causing serious errors for mixtures with relatively high size asymmetry (the size ratio exceeding 2). To overcome this type of problem, Duh and Henderson⁴⁰ proposed an alternative method expressed as

$$b_{ij}(r) = -0.5\{\gamma_{ij}(r)\}^2/\{1 + 0.8\gamma_{ij}(r)\} \quad \text{for } \gamma_{ij}(r) > 0, \quad (2a)$$

$$b_{ij}(r) = -0.5\{\gamma_{ij}(r)\}^2 \quad \text{for } \gamma_{ij}(r) < 0, \quad (2b)$$

where γ_{ij} denotes γ for the i - j pair (components i and j in the mixture considered). Equation (2) and its first and second derivatives with respect to γ_{ij} are continuous at $\gamma_{ij}=0$.

When mixtures have very high size asymmetry, $\gamma_{ij}(r)$ takes very large, negative values at significantly many separations and employing Eq. (2b) gives rise to pathological (abnormally large) $b_{ij}(r)$ at these separations. Therefore, one of us^{35,41} has proposed that Eq. (2b) be replaced by another equation. The resulting method is expressed as

$$b_{ij}(r) = -0.5\{\gamma_{ij}(r)\}^2/\{1 + 0.8\gamma_{ij}(r)\} \quad \text{for } \gamma_{ij}(r) > 0, \quad (3a)$$

$$b_{ij}(r) = -0.5\{\gamma_{ij}(r)\}^2/\{1 - 0.8\gamma_{ij}(r)\} \quad \text{for } \gamma_{ij}(r) < 0. \quad (3b)$$

Just for the L - L pair ($i, j=L$), Eq. (3b) is replaced by

$$b_{ij}(r) = 0.0 \quad \text{for } \gamma_{ij}(r) < 0. \quad (3c)$$

Equation (3) and its first and second derivatives with respect to γ_{ij} are also continuous at $\gamma_{ij}=0$. The reliability of Eq. (3) has been demonstrated for mixtures with high size asymmetry.^{35,41} Further, it has been verified that for mixtures with low size asymmetry the results from Eqs. (2) and (3) are almost indistinguishable. Thus, Eq. (3) provides consistency in the description of a hard-sphere mixture for all size ratios and is best suited to the analysis in this article.

A sufficiently long range R is divided into N grid points ($r_n=n\delta r$, $n=0, 1, \dots, N-1$; $\delta r=R/N$) and all the projections are represented by their values on these points. N and δr are set at 8192 and $0.01d_s$, respectively. The very large set of stiff, nonlinear simultaneous equations is solved using the versatile, highly efficient algorithm developed by Kinoshita and Lado⁴² where the total number of components can arbitrarily be chosen as part of the input data.

C. Density functional theory (DFT)

In the DFT approach, we employ the so-called insertion method⁵ which splits the calculation of the depletion potential into two steps. In the first step we fix one of the large spheres at the origin and make it an external potential for the mixture of small spheres. In this external potential, the M -component fluid mixture of small spheres develops inhomogeneous density distributions $\rho_I(r)$ ($I=1, \dots, M$) which we calculate by minimizing the functional $\Omega[\{\rho_I(r)\}]$ of the grand potential. In order to describe the hard-sphere mixture we use the White Bear version^{37,38} of the fundamental-

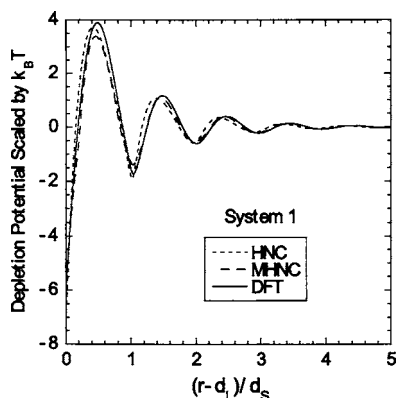


FIG. 1. Depletion potentials between large spheres in system 1 obtained by three different theories: the integral equation theories using the HNC and MHNC closures, respectively, and the DFT.

measure theory (FMT).³⁶ In the second step we insert the other big sphere into the inhomogeneous fluid mixture of small spheres with the help of the potential distribution theorem.

It has been shown⁵ that the depletion potential can be expressed in terms of the one-body direct correlation function of large spheres at the infinite dilution limit for large spheres as follows:

$$\beta W(r) = c_L^{(1)}(r \rightarrow \infty) - c_L^{(1)}(r), \quad (4)$$

where $\beta = 1/(k_B T)$, k_B is Boltzmann's constant, and T is the absolute temperature. The one-body direct correlation function is defined within the framework of the DFT as

$$c_L^{(1)}(r) = -\delta \beta F_{\text{ex}}[\{\rho_I(r)\}]/\delta \rho_L(r), \quad (5)$$

where $F_{\text{ex}}[\{\rho_I(r)\}]$ is the functional of the intrinsic excess free energy. For the calculation of the one-body direct correlation function via Eq. (5), a DFT that is capable of describing a mixture is required. For hard spheres, the system of interest in the present study, the FMT (Refs. 36–38) provides an accurate account for the thermodynamics and the inhomogeneous structure. The quality of the functional was verified in simple⁵ and complex⁹ geometries by comparing DFT predictions with computer simulation data.

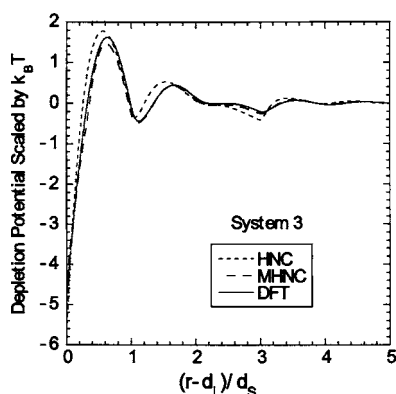


FIG. 2. Depletion potentials between large spheres in system 3 obtained by three different theories, the HNC, MHNC, and DFT.

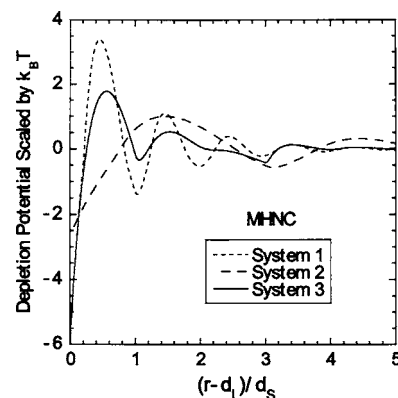


FIG. 3. Depletion potentials between large spheres in systems 1–3 obtained by the MHNC theory.

Like in the IET, the depletion potential obtained by the insertion approach is calculated for all separations of the large spheres in a single calculation, once the density profiles $\rho_I(r)$ ($I=1, \dots, M$) of the small spheres are known.

III. RESULTS AND DISCUSSION

A. Depletion potential in binary mixture

The depletion potentials between large spheres in systems 1 and 3 are shown in Figs. 1 and 2, respectively, for three different theories, the HNC, MHNC, and DFT. The MHNC result is in close agreement with the DFT result, whereas the result from the HNC theory neglecting the bridge functions exhibits significant discrepancy. We note, however, that the HNC result is qualitatively correct and could be satisfactory even in a quantitative sense. The depletion potentials in systems 1–3 are compared in Fig. 3 for the MHNC theory. The periodicities of the depletion potentials in systems 1 and 2 are d_S and $3d_S$, respectively. The periodicity of the depletion potential in system 3 is also d_S . Compared to the potential in system 1, the amplitude of the oscillation of the depletion potential in system 3 is significantly smaller. However, the local-minimum value at $(r-d_L)/d_S \sim 3$ is deeper, which is a remnant of the depletion potential in system 2. The free-energy barrier for large spheres to

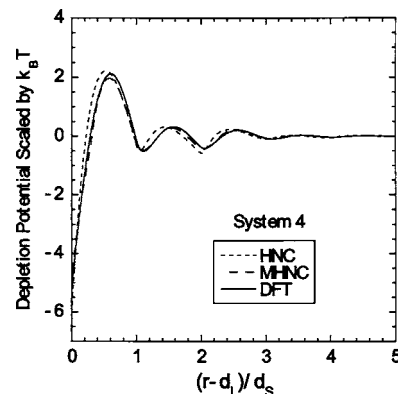


FIG. 4. Depletion potentials between large spheres in system 4 obtained by three different theories, the HNC, MHNC, and DFT.

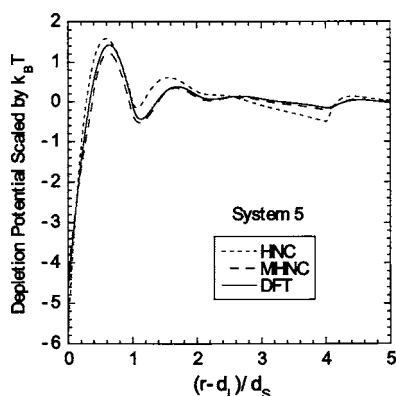


FIG. 5. Depletion potentials between large spheres in system 5 obtained by three different theories, the HNC, MHNC, and DFT.

overcome before reaching the contact in system 1 is in the range of $4.7\text{--}5.7k_B T$. It is lowered in system 3 but still rather high ($\sim 1.9k_B T$).

The depletion potentials in systems 4 and 5 are shown in Figs. 4 and 5, respectively, for the three different theories. Again, the MHNC result is in close agreement with the DFT result while the HNC result exhibits significant discrepancy. This is particularly true for the potential in system 5. By comparing the results shown in Figs. 2, 4, and 5, we can conclude that the free-energy barrier becomes lower as the diameter of the second component increases. However, no further decrease in the barrier seems to be possible in a binary mixture. This necessitates the examination of mixtures comprising more than two or three components.

B. Depletion potential in multicomponent mixture

The depletion potentials in systems 6, 7, and 8 are shown in Figs. 6–8, respectively, for the three different theories considered. Again, the DFT result is much closer to the MHNC result than the HNC result. The free-energy barriers in the depletion potentials in these multicomponent systems are significantly lower than those in the binary mixtures. By comparing the depletion potentials shown in Figs. 6 and 7, we can conclude that the introduction of spheres with intermediate diameters ($1.5d_S$, $2.5d_S$, and $3.5d_S$) only damps the oscillation at large separations ($(r-d_L)/d_S > 1$) and gives no significant reduction of the barrier. The important informa-

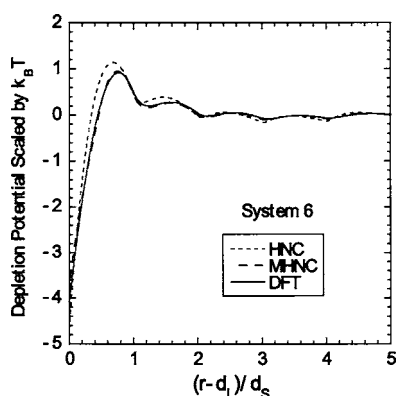


FIG. 6. Depletion potentials between large spheres in system 6 obtained by three different theories, the HNC, MHNC, and DFT.

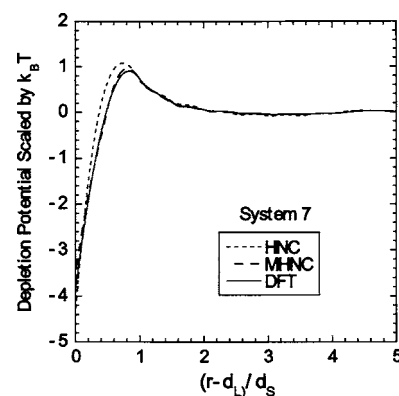


FIG. 7. Depletion potentials between large spheres in system 7 obtained by three different theories, the HNC, MHNC, and DFT.

tion is that as the range in the sphere diameter ($d_S\text{--}4d_S$ in systems 6 and 7 and $d_S\text{--}5d_S$ in system 8) increases, the barrier becomes lower.

The DFT results of the depletion potentials in systems 1 and 8 are compared in Fig. 9. The free-energy barrier in system 1 is $\sim 5.6k_B T$ while that in system 8 is $\sim 0.6k_B T$, which is about an order of magnitude lower and can readily be overcome by the thermal energy. The stabilization free energy in system 8 is $\sim -3.7k_B T$, which is smaller than that in system 1 ($\sim -6.0k_B T$) only by $\sim 38\%$. The depletion potential in system 8 is essentially short ranged and attractive.

The results for the multicomponent mixtures of small spheres can be understood in terms of the packing of small spheres within the space confined between the large sphere surfaces. The concept described in the Introduction has been proven to be valid.

IV. CONCLUSION

We have analyzed the depletion potential between large spheres in a multicomponent mixture of small spheres (up to seven components) using the integral equation theory (IET), in which semiempirical bridge functions are incorporated, and the insertion approach within the framework of density functional theory (DFT). Both theories are capable of treating an arbitrary number of components. The diameters of the

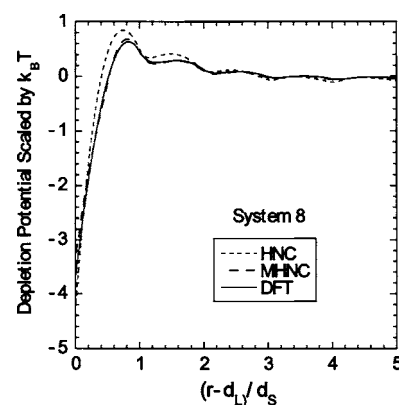


FIG. 8. Depletion potentials between large spheres in system 8 obtained by three different theories, the HNC, MHNC, and DFT.

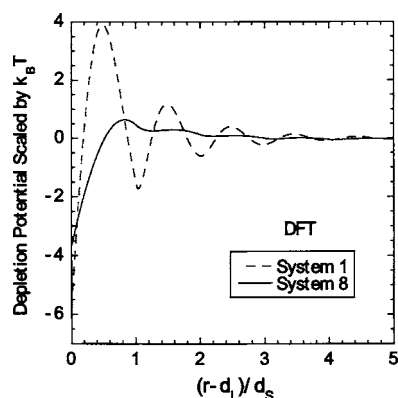


FIG. 9. Depletion potentials between large spheres in systems 1 and 8 obtained by the DFT.

small spheres considered are in the range of d_S-5d_S . The total packing fraction of the small sphere is kept at 0.400, which is fairly high.

A multicomponent mixture with very high size asymmetry presents much challenge because it has not yet been investigated with sufficient details. The IET incorporating our semiempirical bridge functions and the FMT-DFT are significantly different from each other in terms of the approaches and approximations employed. Nevertheless, the results from the two routes are in close agreement with each other. This agreement convinces us of the quantitative validity of our results and, for example, the success of the bridge functions.

The depletion potential in the mixture of small spheres is substantially different from that in a one-component system of equally dense small spheres with diameter d_S . In comparison with the latter, the former is less oscillatory and the free-energy barrier for large spheres to overcome before reaching the contact is significantly reduced. However, this tendency is rather weak in a binary mixture. The most remarkable tendency is observed in a several-component mixture of the small spheres whose diameters are suitably chosen and in which the packing fractions of the components share the same value. The depletion potential in the mixture is essentially a short-ranged attraction with a sufficiently large, negative value at the contact.

The reduction of the free-energy barrier in the depletion potential also reduces the time scale where large spheres reach the contact, which is crucial in biological systems. On the other hand, if the height of the free-energy barrier is of no concern and one can wait for a long time (e.g., several days^{13,14}) for a system to reach its equilibrium state, the integrated strength of the depletion potential can be more important. This integrated strength is measured by the effective second virial coefficient.⁴³⁻⁴⁶

The results from our analysis provide some physical insights into the depletion potential between macromolecules immersed in water molecules and a variety of cosolute molecules. They could also be useful when one attempts to make highly ordered particle arrays on a surface using the colloidal suspension.

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